eV. is the energy required per mole to move a metal ion in a lattice site of the metal crystal at the metal-oxide interface to a vacant site in the cuprous oxide lattice, indicated in Fig. 3. Since the work of removing an ion depends on the crystal face from which it is taken, U_1 might be expected to vary several 0.1 eV. with crystallographic direction. Since diffusion is isotropic in a cubic crystal, variations in U_1 would be directly reflected in W and could be evaluated from the temperature dependence of the variation of effective limiting oxide film thickness with the exposed crystallographic face of the metal. Using the experimental method previously described, the investigation should also yield correlation of contact potential with crystallographic direction for copper–cuprous oxide. This correlation has been evaluated and is reported in a separate paper.[11]

In conclusion some cautionary remarks should be included. Although an expression of the form of Eq. (2) is in good agreement with the low temperature oxidation data on copper, the physical significance of the two parameters, W and especially V, remains somewhat speculative. The general validity of Eq. (2) should be evaluated by studying low temperature gas-oxidation of more metals systematically; some of which form excess semi-conductors (Zn), as well as others forming oxides with no appreciable semi-conductor properties (Al). Furthermore, unless there exist compensating factors hitherto undefined, the Cabrera and Mott hypothesis is based on somewhat idealized surface considerations, seldom, if ever, encountered. As applications of their theoretical treatment accumulate, modifications of Eq. (2) will probably be required to account for structural and other characteristics specific to a given metal–oxide system. Finally, the difficulties in the experimental and theoretical definition of electric contact potential differences in metal–oxide–adsorbed gas systems complicate the independent verification of the values of the parameter, V, derived from their rate analysis.

Acknowledgments.—The author is grateful to N. F. Mott and N. Cabrera for discussions of their views on the oxidation of metal surfaces. He also acknowledges the value of discussions with C. Zener and the assistance of J. Cerny in the preparation of samples. (The research was supported in part by Army Air Force Contract AF-33(038)-6534.)

Summary

The validity of Mott's hypothesis was evaluated by a low temperature study of the oxidation of the cubic face of single crystals of copper in the temperature range 78 to 335° K. By use of a sensitive quartz vacuum microbalance, actual surface areas were determined from microadsorption isotherms and the growth of very thin oxide films were followed with an accuracy of 2%. The rate equation derived from Mott and Cabrera's hypothesis was found to be valid with some limitations for film thicknesses in the range of 5–50 Å. and temperatures from 78 to 300° K.

$$dx/dt = A \exp(x_1/x - W/kT)$$

where x is film thickness at time, t; x_1 is a critical film thickness; W is the energy of activation and A is a temperature independent constant. According to their hypothesis the value of the field accelerating the motion of metal ions through the oxide was found to vary from 10^7 to 10^6 v./cm., the contact potential between copper–cuprous oxide to be 0.83 v. for the (100) face, and the energy of activation for oxidation to be 1.2 eV. Some critical remarks pertinent to the limitations of the hypothesis are included.

CHICAGO 37, ILL. RECEIVED APRIL 17, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, NAVAL RADIOLOGICAL DEFENSE LABORATORY]

The Association of Cerous Ion with Sulfite, Phosphate and Pyrophosphate Ions[1]

BY STANLEY W. MAYER AND S. DAVID SCHWARTZ

Introduction

Measurements of the association between polyvalent cations and inorganic oxygen acids have been made by several investigators.[2,3,4,5] The ion exchange measurements of ion-pair formation between cerous ion and three oxygen acids are reported in this paper.

Experimental

Materials.—Dowex 50[6] resin, 100–200 mesh, was used as the cation exchanger throughout these measurements. The resin was thoroughly washed with 6 *N* HCl, and water. It was then neutralized with sodium hydroxide solution, washed and briefly dried in air.

The purified mixture of Ce^{141}–Ce^{144} fission products, obtained from the Oak Ridge National Laboratory, contained less than 1% of radiochemical impurities.

The water for solutions was boiled to remove carbon dioxide and oxygen. All sodium salts were of reagent grade.

Procedure.—The method was similar to that heretofore employed.[5,7] All equilibrations were carried out at 25 ± 0.5°.

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Atlantic City Meeting, September, 1949.

(2) C. W. Davies, *J. Chem. Soc.*, 2093 (1938); 349 (1939).

(3) B. B. Owen and R. W. Gurry, THIS JOURNAL, **60**, 3074 (1938).

(4) R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).

(5) R. E. Connick and S. W. Mayer, *ibid.*, submitted for publication.

(6) W. C. Bauman and J. Eichhorn, *ibid.*, **69**, 2830 (1947).

(7) E. R. Tompkins and S. W. Mayer, *ibid.*, **69**, 2859 (1947).

Cerous sulfite, phosphate and pyrophosphate are ordinarily insoluble. However, preliminary tests in 0.1 molar solutions showed that the sulfite is soluble at a *p*H below 2.5. Cerous phosphate and pyrophosphate were found to be soluble at a *p*H below 2.2. Accordingly, all the ion exchange equilibrium measurements were made at a *p*H between 1.6 and 2.0, with 10^{-5} molal Ce^{+3}, and with concentrations of polyvalent anion less than 0.02 molal. To prevent large variation in ionic strength, the solutions were made 0.5 molal in $NaClO_4$.

A brief study of the time required to attain equilibrium in exchanges between 10^{-5} molal Ce^{+3} and 0.5 molal $NaClO_4$ was carried out. The data are presented in Fig. 1. Equilibrium was reached within 140 minutes. The equilibration time employed in the measurements with pyrophosphate solutions was 180 minutes. Subsequent equilibrations with these solutions showed that 5% of the pyrophosphate decomposed in five days. This rate of decomposition is in qualitative agreement with that observed by Muus.[8] The equilibration time for the sulfite, phosphate and perchlorate solutions was 3, 16 and 16 hours, respectively.

Results

The notation is identical with that of Mayer and Schwartz.[9] An equilibrium constant, B, is defined by the equation

$$B = \frac{\text{Count}_R\,(Na^+)^3 g_{H_2O} \gamma_{\pm}{}^3{}_{NaClO_4,\,Y}}{\text{Count}_{Aq}\,(Na_R^+)^3 g_R \gamma_{\pm CeCl_3,\,Y}} \qquad (1)$$

where $Y = (Na^+)$. k_m is the concentration quotient for the net reaction between cerous ion and H_aZ^{-b}

$$Ce^{+3} + H_aZ^{-b} = CeH_{(a-d)}Z^{(a+b-3)} + dH^+ \qquad (2)$$

The constancy of the k_m values, over the concentration range investigated, shows that the complex formed contains one oxygen acid anion for each cerium. The concentration of the oxygen acid anion, H_aZ^{-b}, is calculated from the total concentration of H_nZ (the sum of the concentrations of all the anions of H_nZ and the unionized acid) by using the ionization constants and the *p*H's given in the footnotes to the appropriate tables.

Measurement of the moles (d) of hydrogen ion dissociating in reaction (2) was carried out in the following manner. The *p*H of an 0.25 molar solution of cerous chloride was adjusted to 2.00 by adding hydrochloric acid. A 1.50 molar solution of sodium bisulfite was acidified to a *p*H of 2.00. Five milliliters of the cerous chloride was then mixed with five milliliters of the bisulfite solution, and the number of equivalents of 1.00 molar sodium hydroxide required to restore the reaction mixture to a *p*H of 2.00 was determined. By assuming that the number of equivalents of hydroxide required to restore the *p*H to 2.00 (the ionic strength of the mixture was approximately equal to the ionic strength of each of the solutions) was equal to the number of equivalents of hydrogen ion dissociated in the reaction, it was calculated that d equals 0.93 ± 0.02 (four runs) for the reaction of cerous ion with bisulfite ion. A similar set of determinations using 1.50 molar sodium dihydrogen phosphate at a *p*H of 2.00 showed that d equals 2.8 ± 0.1 for the reaction of cerous ion with phosphoric acid. Finally, titration of the mixture of 0.0050 molar cerous chloride and 0.030 molar sodium pyrophosphate with 0.0200 molar sodium hydroxide to restore the *p*H to 2.00 gave the result that d equals 2.7 ± 0.1 for the reaction of cerous ion with trihydrogen pyrophosphate ion.

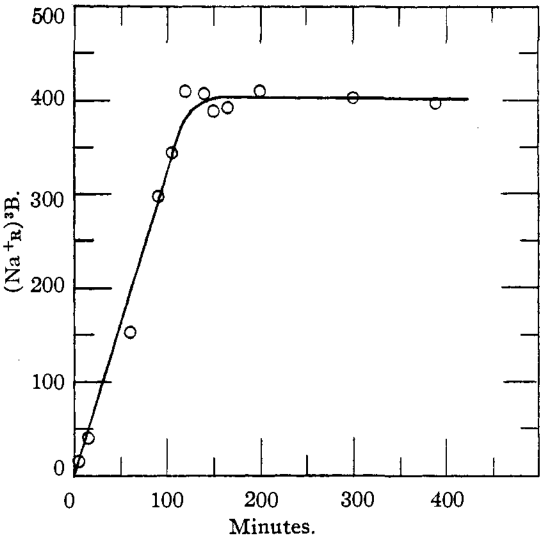

Fig. 1.—Time required to reach equilibrium.

In a series of seven replicate equilibrations between 0.5015 molal sodium perchlorate and 10^{-5} molal cerous perchlorate, B was found to have the mean value 13.7, with a standard deviation of 0.3. The mean activity coefficient of the 0.5015 molal sodium perchlorate is 0.667,[10] and the mean activity coefficient of cerous chloride at that concentration is 0.324.[11]

Data and calculations for the cation exchange equilibrations in the presence of sulfite, phos-

TABLE I

CEROUS SULFITE IN SOLUTIONS OF SODIUM PERCHLORATE AND SODIUM SULFITE[a]

(Na^+)	Resin, g.	Water, g.	$\frac{\text{Count}_R}{\text{Count}_{Aq}}$	Total (H_nSO_3)[b]	k_m
0.516	0.0201	19.8	2.23	0.0080	3.0
.516	.0213	19.8	2.19	.0080	3.7
.515	.0199	19.9	2.25	.0080	2.9
.527	.0201	20.1	1.54	.0160	3.1
.530	.0214	20.0	1.66	.0160	3.1
.529	.0200	20.0	1.55	.0160	3.1
.524	.0203	21.0	1.10	.0286	3.1

[a] 2 *M* Na_2SO_3 solution added to 20.0 ml. of 0.5015 molal $NaClO_4$ solution; *p*H adjusted to 1.69; $\gamma_{\pm NaClO_4} = 0.664 \pm 0.001$, ref. 10; $\gamma_{\pm CeCl_3} = 0.326 \pm 0.001$, ref. 11. [b] Ionization constant of H_2SO_3 = 0.0172, H. V. Tartar and H. H. Garretson, THIS JOURNAL, **63**, 808 (1941).

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[8] J. Muus, *Z. physik. Chem.*, **159A**, 268 (1932).

[9] S. W. Mayer and S. D. Schwartz, THIS JOURNAL, submitted for publication.

[10] J. H. Jones, *J. Phys. Coll. Chem.*, **51**, 516 (1947).

[11] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943; from the data of C. M. Mason, THIS JOURNAL, **60**, 1638 (1938).

TABLE II

CEROUS PHOSPHATE IN SOLUTIONS OF SODIUM PERCHLORATE AND SODIUM DIHYDROGEN PHOSPHATE[a]

(Na^+)	Resin, g.	Water, g.	$\frac{Count_R}{Count_{Aq}}$	Total (H_nPO_4)[b]	$k_m \times 10^5$
0.513	0.0200	19.8	3.14	0.0101	1.4
.513	.0201	19.8	3.06	.0101	1.5
.513	.0201	19.8	2.82	.0101	1.6
.513	.0201	19.8	3.11	.0101	1.4
.525	.0202	20.0	2.62	.0200	1.2
.525	.0200	20.0	2.60	.0200	1.3
.525	.0202	20.0	2.64	.0200	1.2

[a] An acidified 1.00 *M* solution of NaH_2PO_4 was added to 20.0 ml. of 0.5015 molal $NaClO_4$; *p*H of solution = 1.78; $\gamma_{\pm NaClO_4} = 0.664$, ref. 10; $\gamma_{\pm CeCl_3} = 0.325$, ref. 11. [b] Ionization constant of $H_3PO_4 = 7.52 \times 10^{-3}$, L. F. Nims, THIS JOURNAL, 56, 1110 (1934).

TABLE III

CEROUS PYROPHOSPHATE IN SOLUTIONS OF SODIUM PERCHLORATE AND SODIUM PYROPHOSPHATE[a]

(Na^+)	$\frac{Count_R}{Count_{Aq}}$	Total $(H_nP_2O_7) \times 10^4$	*p*H	Fraction $H_3P_2O_7^-$[b]	k_m
0.498	2.73	0.99	1.60	0.45	0.16
.498	2.77	.99	1.60	.45	.15
.498	2.87	.99	1.60	.45	.12
.498	2.91	.99	1.60	.45	.10
.494	2.54	1.96	1.60	.45	.13
.494	2.81	1.96	1.60	.45	.09
.494	2.44	1.96	1.60	.45	.15
.494	2.58	1.96	1.60	.45	.12
.498	1.118	9.3	1.64	.43	.15
.498	1.204	9.3	1.64	.43	.13
.497	1.233	9.3	1.64	.43	.13
.498	1.250	9.3	1.64	.43	.12
.489	0.790	18.2	1.62	.44	.14
.491	.666	18.2	1.70	.41	.12
.489	.630	18.2	1.76	.38	.10
.488	.647	18.2	1.70	.41	.13

[a] An acidified solution of $Na_4P_2O_7$ was added to 20.0 ml. of 0.5015 molal $NaClO_4$; $g_R = 0.0201 \pm 0.0002$; $g_{H_2O} = 20.5 \pm 0.3$; $\gamma_{\pm NaClO_4} = 0.667 \pm 0.001$, ref. 10; $\gamma_{\pm CeCl_3} = 0.324 \pm 0.001$, ref. 11. [b] Ionization constants are: 0.14 for $H_4P_2O_7$, 0.011 for $H_3P_2O_7^-$, and 2.1×10^{-7} for $H_2P_2O_7^{-2}$, D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, Chapter 6.

phate and pyrophosphate are summarized in Tables I, II and III.

Discussion

Calculation of Association Constants.—In the process of ion association one step consists of the momentary formation of complexes such as $CeH_3PO_4^{+3}$, $CeH_2PO_4^{+2}$ and $CeHPO_4^+$. It has been pointed out by Connick and McVey[4] that the presence of a highly charged ion, such as Ce^{+3} makes the complex acid strong so that H^+ dissociates from it. Ricci[12] has developed the empirical relationship[13]

$$pK = 8.0 - m\ (9.0) + n\ (4.0) \tag{3}$$

where *m* is the formal charge on the central atom of the acid and *n* is the number of oxygens with unit formal charge. Equation (3) can be employed to estimate the ionization constant of such complex oxy-acids. The ionization constant of $CeHPO_4^+$ is estimated to be approximately 10, while the ionization constants of $CeH_2PO_4^{+2}$ and $CeH_3PO_4^{+3}$ would be larger. Therefore, at a *p*H of 1.6, more than 99% of these complex acids dissociate to $CePO_4$. Similiarly, the ionization constant of $CeHSO_3^{+2}$ is greater than 10^2 and practically complete dissociation to $CeSO_3^+$ takes place. The ionization constant of $CeHP_2O_7$ is estimated to be 0.14. Consequently, more than 94% of this complex is ionized to $CeP_2O_7^-$.[14]

Therefore, the major reactions of Ce^{+3} in the solutions investigated are

$$Ce^{+3} + HSO_3^- = CeSO_3^+ + H^+ \tag{4}$$

$$Ce^{+3} + H_3PO_4 = CePO_4 + 3H^+ \tag{5}$$

$$Ce^{+3} + H_3P_2O_7^- = CeP_2O_7^- + 3H^+ \tag{6}$$

The concentration quotient for each of these is listed in the second column of Table IV. The calculation of the activity coefficient quotient, k_γ, involves assumptions relative to the mixed electrolyte activity coefficients. The empirical relationship[5]

$$\gamma^{x+1}_{\pm\,(ClO_4)_x} \text{ in } Y \text{ molal } NaClO_4 = \gamma^{x}_{\pm NaClO_4,\,Y}\ \gamma_{\pm M(ClO_4)_x,\,Y} \tag{7}$$

where *x* is the charge on the cation *M*, was utilized for this calculation. The association constant, K_a, is tabulated in the last column of Table IV. K_a is equal to the product of k_a and the association constant of the oxy-acid anion in reactions (4), (5) and (6).

TABLE IV

CONSTANTS FOR ION-PAIR FORMATION BETWEEN CEROUS ION AND OXYGEN ACIDS FOR SULFUR AND PHOSPHORUS

Ion pair	k_m	k_γ	k_a	K_a
$CeSO_3^+$	3.2 ± 0.2	2.2	7.0	1.1×10^8[b]
$CePO_4$	$(1.4 \pm 0.1) \times 10^{-5}$	1.2	1.7×10^{-5}	3.4×10^{18}[c]
$CeP_2O_7^-$	0.12 ± 0.02	1.2	0.14	1.4×10^{17}[d]
$CeSO_4^+$	60[a]	1.4	84	8.4×10^1

[a] R. E. Connick and S. W. Mayer, THIS JOURNAL, submitted for publication. [b] Constant for $H^+ + SO_3^{-2} = 1.6 \times 10^7$, H. V. Tartar and H. H. Garretson, *ibid.*, **63**, 808 (1941). [c] Constant for $3\ H^+ + PO_4^{-3} = 2 \times 10^{23}$, K. S. Pitzer, *ibid.*, **59**, 2365 (1937). [d] Constant for $3\ H^+ + P_2O_7^{-4} = 1.0 \times 10^{18}$, D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, Chapter 6.

Applicability of Bjerrum's Theory for Ion-Pair Formation.—Bjerrum[15] has hypothesized that the coulombic forces of the ions acting over the distance of closest approach, $\mathring{a}$, determine the association constant of an ion-pair. With

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[12] J. E. Ricci, THIS JOURNAL, **70**, 109 (1948).

[13] Ricci's empirical rule can be derived on the theoretical bases of A. Kossiakoff and D. Harker (*ibid.*, **60**, 2047 (1938)) whose calculations for $H_2PO_4^-$ can be arranged to the form: ΔF ionization = (10.6 − 12.4 *m* + 4.9 *n*) kcal. Therefore, $pK = 7.8 - 9.1\ m + 3.6\ n$.

[14] Recently, L. B. Rogers and C. A. Reynolds (*ibid.*, **71**, 2081 (1949)) postulated that trivalent cations form the ion-pair $M^{III}P_2O_7^-$ in dilute solutions of pyrophosphate.

[15] N. Bjerrum, *Kgl. Danske Videnskab. Selskabs*, **7**, no. 9 (1926); R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

4.4 Å. as the distance of closest approach,[16] Bjerrum's formulation yields association constants of: 3.7 for $CeSO_3^+$ and $CeSO_4^+$; 71 for $CePO_4$; 2.2 × 10^3 for $CeP_2O_7^-$. The disagreement between these values and the K_a's of Table IV is large. The experimental K_a's of $CeSO_3^+$ and $CeSO_4^+$ are not equal, but differ by a factor greater than 10^6. Furthermore, the K_a of $CePO_4$ exceeds that of $CeSO_3^+$ by a factor of more than 10^{10}. It appears that Bjerrum's hypothesis is not sufficient to account for the observed association constants.

Comparison of Association Energies of Oxy-acids and Cerous Ion-Pairs.—The data of Table V show that the energy of association of the ion-pairs formed by Ce^{+3} and the listed anions parallels to some extent the energy of association of the first hydrogen ion with the corresponding anions. The energy correlation between the fully associated acids (H_2SO_3, H_3PO_4 and $H_4P_2O_7$) and the Ce^{+3} ion-pairs is better, possibly because the numbers of charges involved in the associations are more nearly equal.

This correlation suggests the hypothesis that the mechanism of ionization of the Ce^{+3} ion-pairs is similar to that of the oxy-acids. Several investigators,[12,13,17] have proposed that the formal charges on the atoms of non-resonating oxygen acids are important in determining the ionization constants of those acids. Kossiakoff and Harker[13] hypothesize that the ionization mechanism of the acids consists of the separation of H^+ "from the anion to a water molecule followed by the subsequent exchange" of H^+ between water molecules until the H^+ is beyond the field of the anion. Similarly, it can be postulated that the ionization of the Ce^{+3} ion-pairs consists of the separation of the cation from the anion, followed by diffusion of the Ce^{+3} beyond the significant range of the attractive forces of the anion.

TABLE V

ENERGY OF ASSOCIATION OF SEVERAL ACIDS AND ION PAIRS[a]

Anion	$-\Delta F$, first associated H^+	$-\Delta F$, fully associated acid	$-\Delta F$, Ce^{+3} ion pairs	$-\Delta F$, Zr^{+4} ion pairs[e]
SO_3^{-2}	9.9[b]	12.2[b]	11.0	..
PO_4^{-3}	17.7[b]	31.8[b]	25.3	34
$P_2O_7^{-4}$	14.5[b]	25.7[b]	23.4	..
SO_4^{-2}	2.6[c]	...	2.5	6.7
F^-	4.3[d]	4.3[d]	5.5	12

[a] Energy of association = $-\Delta F_{\text{association}}$ (in kcal.). [b] See association constants in footnotes to Table IV. [c] W. J. Hamer, THIS JOURNAL, 56, 860 (1934). [d] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, Chapter 3. [e] R. E. Connick and W. H. McVey, THIS JOURNAL, 71, 3182 (1949); R. E. Connick and W. H. Reas, AECD-2491 (1949).

It has been calculated[13] (with $H_2PO_4^-$ employed as a representative non-resonating oxy-acid) that the energy of association of H^+ increases by approximately 12.4 kcal. for each unit decrease in formal charge (m) on the central atom of the anion, and that it increases by about 4.9 kcal. per unit increase in the number (n) of H^+ ions that have dissociated. For Ce^{+3}, the corresponding increases in the energy of association would be approximately 37 and 15 kcal. On the other hand, Bjerrum's theory predicts for Ce^{+3} ion-pairs an increase of only 1.9 kcal. per unit decrease in the charge of the anion.

It appears that the possibility that the cation in the acid or ion-pair may be associated with water has not been fully considered in both these mechanisms. Thus, the ionization might be more precisely written

$$H_3(aH_2O)PO_4 = H^+(bH_2O) + H_2(cH_2O)PO_4^- \quad (8)$$

where the energy of hydration of the products is generally greater than the energy of hydration of the associated acids. The energy of hydration for individual ions is very large.[18] Consequently, the decrease in the energy of ionization due to the unknown increase in the energy of hydration during ionization can well be of the same order of magnitude as the energy of ionization arising from the formal charges of the atoms.[19]

Correlation among Ion-Pairs of Zr^{+4} and Ce^{+3}.—Connick, McVey and Reas[6,20] have pointed out several factors which cause them to question the accuracy of their measurements of the association constants of several ion-pairs of zirconium. Nevertheless, there apparently is some correlation in Table V in that the association energy for the zirconium ion-pair is consistently several kcal. higher than for the corresponding cerous ion-pair or associated acid.[21] The greater energy of association for zirconium is in qualitative agreement with Bjerrum's hypothesis and the formal charge concept. The uncertainty with regard to the change in the energy of hydration during ion-pair formation precludes an exact evaluation of the relative contribution of Bjerrum's forces and the formal charges.

The energy of association for alkaline earth sulfate ion-pairs is approximately 0.4 kcal.[1] As anticipated, this energy is less than that for $CeSO_4^+$ or $ZrSO_4^{+2}$. No other association constants for alkaline earth ion-pairs with non-

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[16] Based on $\mathring{a}$ = 3.9 for $LaCl_3$ (T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **61**, 200 (1939)) as modified by the difference between the ionic radius of Cl^- and the radii of these oxy-acids (L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, Chapter 7).

[17] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, Chapter 6.

[18] 60 kcal. to more than 400 kcal., W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, Chapter 2.

[19] Differences in the change of energy of hydration during ionization may explain discrepancies in some of the predicted ionization constants of acids and variations in the association constants among simple ions of identical formal charges.

[20] R. E. Connick and W. H. Reas, AECD-2491 (1949).

[21] The similarity between the relationships among the constants for fluoride ion-pairs and oxy-acid ion-pairs suggests that the correlation may extend to other weak non-resonating acids. The tabulated values for the energies of association of CeF^{+2} and ZrF^{+3} agree qualitatively with those for the association of FeF^{+2} and ThF^{+3} (H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949)).

resonating acids were found in the chemical literature. It would seem desirable to attempt to measure the association constants for other ion-pairs of the alkaline earths, particularly in view of the fact that the solubility of their hydroxides (in contrast to $Ce(OH)_3$) may allow measurements at high *p*H for oxy-acids having a formal charge of zero.

Summary

1. The distribution of cerous ion between ion exchange resin and solutions of sulfurous, phosphoric and pyrophosphoric acids has been measured.

2. The constants for the reaction between Ce^{+3} and these acids have been calculated.

3. The association constants for $CeSO_3^+$, $CePO_4$ and $CeO_2O_7^-$ are 1.1×10^8, 3.4×10^{18} and 1.4×10^{17}, respectively.

4. Bjerrum's theory for ion-pair formation does not predict these association constants.

5. A correlation between the association of oxy-acid anions with H^+ and their association with Ce^{+3} has been pointed out.

SAN FRANCISCO 24, CAL. RECEIVED APRIL 11, 1950

[CONTRIBUTION FROM THE UNIVERSITY LABORATORY OF PHYSICAL CHEMISTRY RELATED TO MEDICINE AND PUBLIC HEALTH, HARVARD UNIVERSITY]

Light Scattering Studies of a Polystyrene Latex[1a]

BY WALTER B. DANDLIKER[1b]

The size and shape of the particles in a polystyrene latex (Dow Latex 580-G, Lot 3584) have been studied by various methods in a number of laboratories.[2] The particles have been found to be spheres with a number average diameter of 2590 Å. and have a distribution of size over only an extremely narrow range. Since this material has been used as a means of determining absolute lengths in the electron microscope, it is desirable to have as many independent measurements of particle size as possible. The fact that this latex is nearly monodisperse and that the particles are spherical suggests that additional valuable information can be obtained by light scattering. The exact solution to the problem of light scattering from such spheres is provided by the Mie theory.[3] Several recent reviews[4,5,6] concerning the Mie theory summarize the theoretical and experimental work dealing with light scattering from large spheres, and provide bibliographies to this subject.

In general, the optical properties of a sphere depend upon its relative refractive index m and the value of $\alpha = 2\pi r/\lambda$ where r is the radius of the sphere and λ is the wave length of the light in the surrounding medium. These parameters determine the magnitude, the angular distribution, and the polarization of the scattered intensities which together characterize completely the scattering from an isolated particle. We shall limit our considerations to the horizontal plane containing the incident and scattered beams and shall specify the direction of scattering by ϑ, the angle between the directions of propagation of the incident and scattered rays. The angular distribution can be represented conveniently by the function $P^{-1}(\vartheta)$ which gives reciprocal relative intensities of the vertical component (electric vector vertical) in the scattered light with unpolarized incident light. These reciprocal intensities have been normalized to unity at $\vartheta = 0$. The function $P^{-1}(\vartheta)$ has been plotted against $\sin^2 \vartheta/2$.

Determination of Particle Size from the Angular Position of Minimum Intensity.—Since the positions of minimum intensity in an angular dependence curve are functions of both m and α, the location of these positions ($\vartheta_{\text{Min.}}$) can be used to determine the size of a sphere. This method is similar to one employed by LaMer and Sinclair[7] in studying aerosols and by Johnson and LaMer[8] in measuring the particle size of sulfur hydrosols. These studies have been extended in a series of papers and include measurements carried out in the presence of true absorption.[9] Figure 1 shows ϑ_{Min} (for first order interference) as a function of m for different values of α. The points for $m = 1$ were obtained from the analytical expression given by Debye.[10] The problem of scattering from spheres of small refractive index was earlier solved by Rayleigh.[11] The remaining values were estimated graphically from plots of $P^{-1}(\vartheta)$ using the tabulated values of LaMer and Sinclair[12] for the intensity distribution

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(2) A sample of this latex was kindly supplied by Dr. Robley Williams and Dr. R. C. Backus of the University of Michigan. They have determined (THIS JOURNAL, **71**, 4052 (1949)) the size distribution curve by electron microscopy.

(3) G. Mie, *Ann. der Physik*, **25**, 377 (1908).

(4) H. C. van de Hulst, "Optics of Sperical Particles," Duwaer and Sons, Amsterdam, 1946.

(5) G. Oster, *Chem. Rev.*, **43**, 319 (1948).

(6) D. Sinclair and V. K. LaMer, *ibid.*, **44**, 245 (1949).

(7) V. K. LaMer and D. Sinclair, N. D. R. C., Report 57 (1941) and 1668 (1943); personal communication from Professor LaMer.

(8) I. Johnson and V. K. LaMer, THIS JOURNAL, **69**, 1184 (1947).

(9) A. S. Kenyon and V. K. LaMer, *J. Colloid Sci.*, **4**, 163 (1949).

(10) P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).

(11) Lord Rayleigh, *Proc. Roy. Soc.* (*London*), **A90**, 219 (1914).

(12) V. K. LaMer and D. Sinclair, "Verification of Mie Theory" O. S. R. D. Report No. 1857 (1943).